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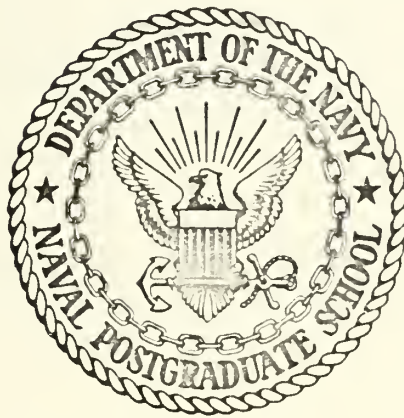
AN ANALYSIS OF THE CONCENTRATIONS OF
HEAVY METALS IN MONTEREY HARBOUR
UTILIZING THE METHODS OF ATOMIC
ABSORPTION SPECTROPHOTOMETRY
AND POLAROGRAPHY

James William Tanner

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Monterey, California



THESIS

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ATOMIC ABSORPTION SPECTROPHOTOMETRY
AND POLAROGRAPHY

by

James William Tanner

Thesis Advisor:

E. C. Haderlie

DEC 1971

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An Analysis of the Concentrations of Heavy Metals
in Monterey Harbour Utilizing the Methods of
Atomic Absorption Spectrophotometry and Polarography

by

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Ensign, United States Naval Reserve
B.S., University of Illinois, 1970

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN OCEANOGRAPHY

from the

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December 1971

ABSTRACT

As part of the Monterey Breakwater Project, six water samples were taken from the study area located offshore from Del Monte Beach east of Municipal Wharf No. 2 in Monterey, California. The heavy metals in the sea water were concentrated and removed using the ammonium pyrrolidine dithiocarbamate (APDC) -- methyl isobutyl ketone (MIBK) solvent extraction system. The concentrations of the metals cobalt, copper, iron, lead, and nickel in the samples were determined using atomic absorption spectrophotometry. It was found that the APDC-MIBK solvent extraction system was not adequate for analysis by polarography.

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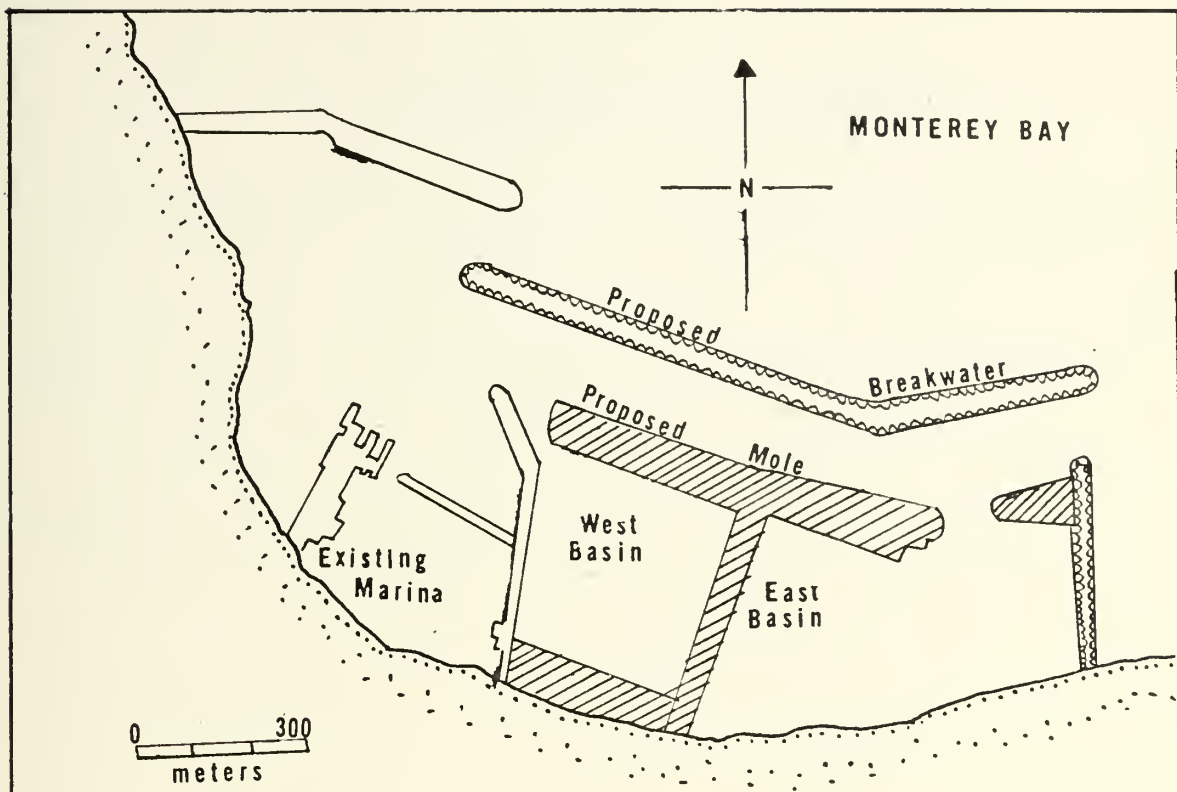
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ml	milliliters
mV	millivolts
ppm	parts per million
ppb	parts per billion
μ A	microamperes

I. INTRODUCTION

In 1972 or 1973 construction may begin on a breakwater (Figure 1.) to be located off of Del Monte Beach north and east of the present Municipal Wharf No. 2 in Monterey, California (Haderlie 1971). Faculty and students of the Naval Postgraduate School have undertaken to describe the ecology of this area before construction is commenced. Ecological base lines in the undisturbed area will be established so that environmental changes brought about by harbour construction can be evaluated. A series of ecological transects have been placed across the study area, and fifteen stations have been located along these transects (Figure 2). At each of these stations the bottom sediment and benthic infauna are periodically examined and vertical plankton tows are taken.

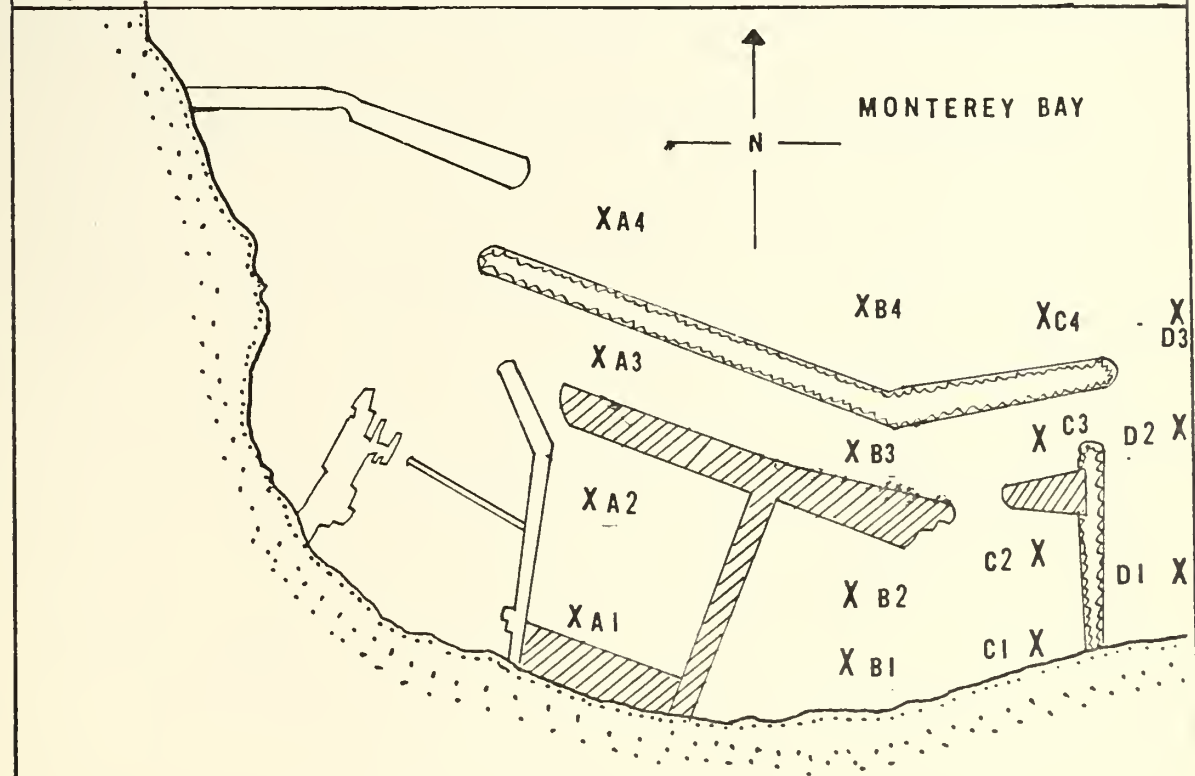
As part of this study water samples were taken at selected stations and analysed for the heavy metals cobalt, copper, iron, lead, and nickel by atomic absorption spectroscopy and by polarography. The results obtained by these two methods are compared and discussed.



Plan for Breakwater Construction

Haderlie(1971)

Figure 1



Ecological Transects

Haderlie(1971)

Figure 2

II. DESCRIPTION OF PROBLEM

The elements cobalt, iron, lead, and nickel occur in sea water in such minute quantities that sensitive and accurate analytical techniques are needed for determining the abundance of these metals.

Brooks et al. (1967) suggest that neutron activation, isotope dilution and atomic absorption spectrophotometry are the most reliable methods for analysis of trace metals in water. For the present study the methods of atomic absorption spectrophotometry and polarography were chosen for analysing the concentrations of these metals in the samples obtained from the water off Del Monte Beach.

A. PRINCIPLES OF ATOMIC ABSORPTION

In atomic absorption spectrophotometry the elements to be determined are dissociated from their chemical bonds and converted into an atomic vapor by burning the sample in a flame (Kahn 1968). The elements in this vapor exist in an unexcited, unionized ground state. When light of a wavelength which is characteristic of the desired element is passed through the vapor, some of it is absorbed as the electrons of the elements under analysis are excited from the ground state to a higher energy level.

The source of radiation for atomic absorption is a hollow cathode lamp filled with low pressure neon or argon. The spectrum emitted by such a lamp consists only of the spectrum of the filler gas and of

the element being sought. The desired element in the atomic vapor absorbs radiation from this spectrum at the wavelengths which correspond to transitions from the ground state to a higher energy level. The amount which is absorbed is proportional to the concentration of the desired element in the sample being determined.

After passing through the flame, the beam passes through a filter or monochromator which screens out the unwanted portions of the spectrum (Figure 3). A photodetector then measures the intensity of the light at the desired wavelengths. The absorbance of the unknown samples is compared to that of standards of known concentration to determine the unknown concentration.

1. Advantages of Atomic Absorption Spectrophotometry

Kahn (1968) has summarized the advantages of atomic absorption. The required equipment is moderate in cost and relatively simple to operate. Low detection limits and high precision and accuracy make the technique useful for determination of about 65 elements in a variety of matrices. There are almost no spectral interferences and few chemical interferences with the method. As a result, chemical separations are seldom needed or are simple to perform when they are necessary.

Further advantages are suggested by Lewis (1969). These are the specificity of analysis, the capability of determining many elements in the same solution with the same instrument and the increased speed of analysis. In addition he states that atomic

absorption also provides the possibility of obtaining data output in direct readout form.

Another advantage is the insensitivity of atomic absorption methods to temperature changes in the vapor-producing environment relative to atomic emission methods. This is due to the fact that temperature changes cause an exponential change in the number of atoms capable of emitting light while having very little effect on the number of atoms capable of absorbing (Slavin 1968).

2. Disadvantages of Atomic Absorption Spectrophotometry

The disadvantages of atomic absorption spectrophotometry have been discussed by Lewis (1969). The standard solutions must be prepared in the same matrix as the unknown samples. Due to the few interferences that do occur, it is sometimes necessary to carry out chemical separations. Since atomic absorption work is performed in dilute solutions, losses due to adsorption on the walls of containers and contamination from reagents and containers contribute errors to the method. Losses of trace elements due to adsorption are reduced by using containers of polyethylene, which has been found to be one of the best container materials because of its nonpolar nature and low content of metals. Contamination is lessened by adhering to simple methods whenever possible.

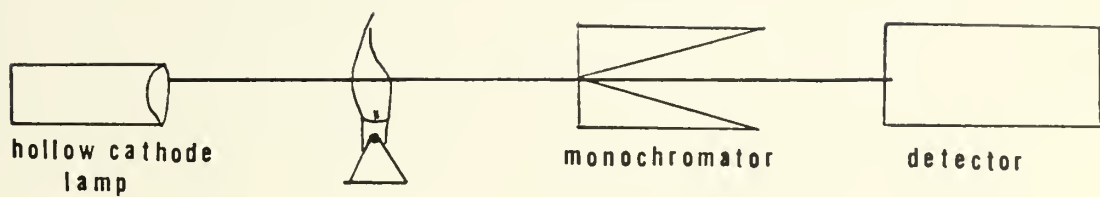


Figure 3

Kahn (1968)

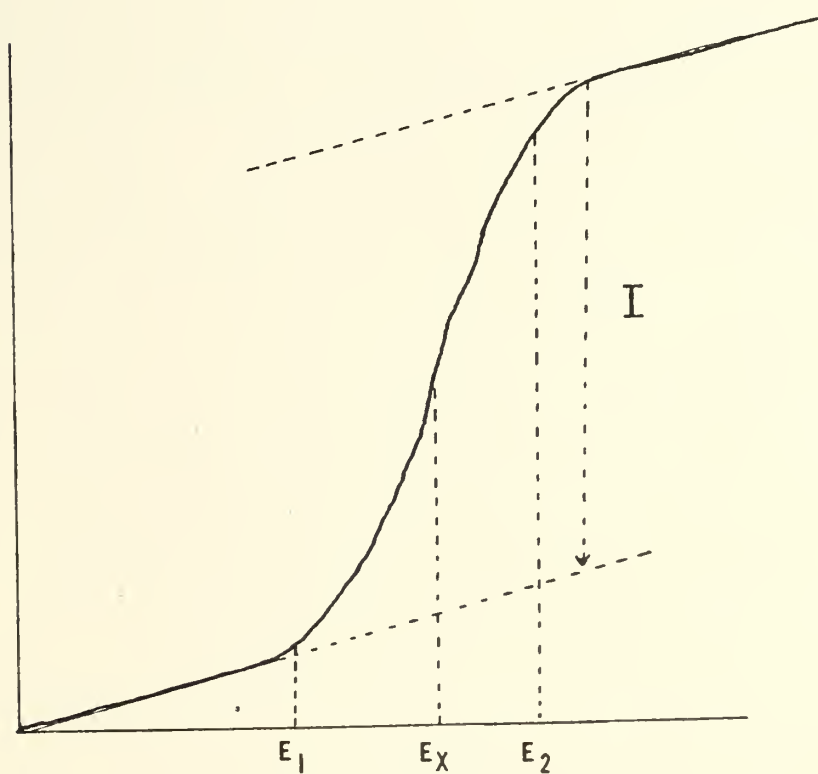


Figure 4

Pinta (1970)

B. PRINCIPLES OF POLAROGRAPHY

Polarography is an electrochemical method of analysis in which electrolysis takes place between two electrodes in the solution to be determined (Pinta 1970). The reference electrode is kept at a constant potential, while the indicator electrode is subjected to a varying potential. As the potential of the indicator electrode is increased, the current which passes through the solution is originally small but is slowly increasing (Figure 4). At the minimum decomposition voltage of the electrolyte (E_1) the current starts to increase swiftly and linearly. As this current increases, the number of ions reduced (or oxidized) per unit time increases. These ions are replaced at the electrode by diffusion. At the saturation or diffusion current, the number of ions reduced at the electrode equals the number of ions reaching it by diffusion. At this point the current returns to a slowly increasing state. A graph of current intensity versus potential resembles the S-shaped curve. The inflection point of the curve is the reduction potential (E_x) of the particular ion being examined and identifies that ion. The amount of the ion which is present is proportional to the height of the S-shaped curve.

1. Advantages of Polarography

The main advantage of polarography is the speed with which analysis can be performed (Tikhonov and Zhavoronkina, 1963). The sensitivity and selectivity of the electrode processes minimize interferences (Maienthal and Taylor, 1968). Thus chemical

separations are seldom necessary. As a result several elements can often be analysed at the same time in the same supporting electrolyte.

2. Disadvantages of Polarography

Pinta (1970) mentions several disadvantages of polarographic technique. Since temperature influences diffusion, it must be held constant during a series of determinations. Similarly, the solution must not be allowed to move as this would effect the diffusion region of the ions. A supporting electrolyte is needed to prevent the displacement of ions by migration, and impurities in this supporting electrolyte could contaminate the solution. If the reduction potentials of the ions in the solution are not separated by at least 150 mV interference will occur and the offending ions must be chemically separated.

C. SCOPE OF ANALYSIS

Polarography determines the concentration of the ionized species of a particular element which are present in the solution (Pinta 1970). Atomic absorption, however, gives a total analysis of all forms of the element being determined without regard to the different species present (Burrell 1968).

D. USE OF SOLVENT EXTRACTION IN THE ANALYSIS OF SEA WATER FOR TRACE ELEMENTS BY ATOMIC ABSORPTION

Fabricand et al. (1962) determined trace elements with atomic absorption by direct aspiration of raw sea water into the burner flame. These results do not seem to have been reproduced by other investigators

for the elements studied (Brooks et al. 1967). The mean values in the sea water of the concentrations of cobalt, copper, iron, lead, and nickel are below the detection limits of present-day equipment (Burrell 1968). Therefore, some form of pre-analysis concentration is required.

The most commonly used methods of concentration are co-precipitation, solvent extraction and the use of ion exchange columns (Burrell 1967). There are several advantages to the method of chelation and solvent extraction of trace metals for atomic absorption analysis. This technique provides a simple separation of the sample into ionic and complex-bound fractions. The necessary reagents are easily purified, and contamination of the sample is lessened by the simplicity of the procedure. Finally, the use of an organic solvent increases the sensitivity of the instrument as much as three to five times, since it allows more of the sample to reach the flame. This is due to the formation of more small-sized droplets during aspiration of the organic than during aspiration of an aqueous solvent. These smaller droplets are better able to pass through the burner mixing chamber without condensing. The exact amount of this increase in absorption depends on the solvent being aspirated. (Mulford 1966).

1. Principle of Solvent Extraction

Solvent extraction is the procedure in which two immiscible liquids are shaken together so as to bring about a transfer of one or more constituents from one of the phases to the other (Mulford 1966). Usually one of the phases is an aqueous solution and the other is an

organic solvent. Since metal salts are usually more soluble in the aqueous phase, they must be converted into uncharged species so that they may be extracted into the organic moiety. This is done by allowing the metal to form a complex with a chelating agent. These complexes are usually stable, neutral, and extractable into organic solvents. An appropriate solvent must completely dissolve the metal complex and be immiscible with the solution which is being extracted. Also, the organic solvent should exhibit good burning characteristics in the spectrophotometer flame.

2. The APDC-MIBK Solvent Extraction System

Several workers have reported satisfactory results for trace metal determinations of sea water with a solvent extraction system using ammonium pyrrolidine dithiocarbamate (APDC) as the chelating agent and methyl isobutyl ketone (MIBK) as the extractant (Brooks et al. 1967, Burrell 1967, Burrell 1968, Mulford 1966, Sprague and Slavin 1964). Cobalt, copper, iron, lead, nickel and zinc have been extracted from sea water using this method. Its usefulness consists of its non-specificity of extraction and excellent combustion characteristics (Burrell 1968). When the element is in the organic phase the detection limits are improved about four times (Sprague and Slavin 1964). The present study uses the APDC-MIBK solvent extraction system developed by Brooks et al. (1967).

E. USE OF SOLVENT EXTRACTION IN THE ANALYSIS OF SEA WATER FOR TRACE ELEMENTS BY POLAROGRAPHY

Conventional polarography with a dropping mercury electrode attains a sensitivity of 10^{-5} M. (Maienthal and Taylor, 1968). The elements to be determined occur in sea water in concentrations on the order of 10^{-6} M. consequently the samples must be concentrated prior to analysis. The APDC-MIBK solvent extraction system was used to remove the heavy metal ions from the sea water into the organic solvent. It was then attempted to dissociate the metal ions from the APDC-metal complexes by shaking the organic solution with a strongly acidic aqueous solution which would take up the freed metal ions. The concentrations of the desired trace elements in this solution were then determined by polarography.

III. EXPERIMENTAL PROCEDURE

A. SAMPLING

Samples of sea water were taken from the Research Vessel, *Acania*, on 3 November 1971 at six selected stations on the ecological transects of the Monterey Breakwater Project (Figure 2). The water was collected in a five liter polyvinyl chloride van Dorn bottle and stored in large five gallon polyethylene jugs. Soon after collection the samples were filtered through a 0.45 micron Millipore filter to remove particulate matter. This precaution was taken to prevent adsorption of the trace metals on the particulate matter in the water during storage (Burrell 1967). Spencer and Brewer (1969) report that filtered sea water has been stored for periods of up to three months without appreciable change in the concentrations of dissolved metals.

B. ANALYSIS BY ATOMIC ABSORPTION

1. Extraction Procedure

The APDC-MIBK extraction system of Brooks et al. (1967) was utilized. This technique uses a sea water/solvent ratio of 750:20 and compensates for any incomplete extraction of the elements from the sea water samples.

a. Reagents and Equipment

The reagents needed in the extraction procedure were purified before use. Distilled water, reagent grade 6N hydrochloric acid and commercial grade methyl isobutyl ketone were redistilled from an all glass still. The 1% aqueous solution of APDC was shaken with an equal volume of MIBK, and the lower aqueous phase was separated and used. Since complexes of APDC and metal contaminants are much more soluble in MIBK than is APDC alone, these complexes were preferentially taken into the organic phase, which was discarded. The standard aqueous solution consisted of 20 parts per million each of cobalt, copper, iron, lead and nickel in double distilled water. Commercial standards (1000 parts per million; Beckman Instruments, Inc.) were used for cobalt, copper, iron and nickel. The lead standard was prepared from lead nitrate.

To reduce contamination all laboratory glassware and the polyethylene bottles were rinsed with redistilled hydrochloric acid, tap water, 1% aqueous APDC, and double distilled water, in that order.

b. Extraction

Extraction was carried out at the pH of sea water (pH8). 750 ml. samples of filtered sea water were placed in 100ml. polyethylene bottles and 35 ml. of MIBK and 7ml. of the 1% APDC solution were added to each bottle. The samples were then placed on a mechanical shaker and equilibrated for 30 minutes. After equilibration the samples were placed in separatory funnels to effect phase separation,

and the organic phases were stored in polyethylene bottles until analysis.

The preparation of the working curve (Figures 5 and 6) required that the extracted sea water be as free as possible from the trace elements being determined. To this end a further 20 ml. of MIBK were added to the extracted aqueous phases. The samples were equilibrated on the mechanical shaker for an additional five minutes, and the phases were separated. The organic phases were discarded and the aqueous phases were recombined to ensure homogeneity. Four 750 ml. samples of this water were replaced in the bottles, and incremental amounts of the 20 parts per million standard solution were added to give concentrations of 0, 2, 5, and 10 parts per billion of the five elements in the sea water. The temperature of the water was found to be 20 degrees Centigrade. Using the data of Brooks et al. for the solubility of MIBK in sea water as a function of temperature, it was found that 20.8 ml. of MIBK remained after the first equilibration. To extract the standard solutions, 20.8 ml. of MIBK and 7 ml. of the 1% APDC solution were added to each bottle, and the bottles were shaken for 30 minutes and the phases separated as before. The organic phases from this extraction and from the first extraction were aspirated into the flame of the spectrophotometer for analysis.

2. Instrumental Procedure

The instrumental analysis was performed with a Perkin-Elmer 303 Atomic Absorption Spectrophotometer with a triple slot burner

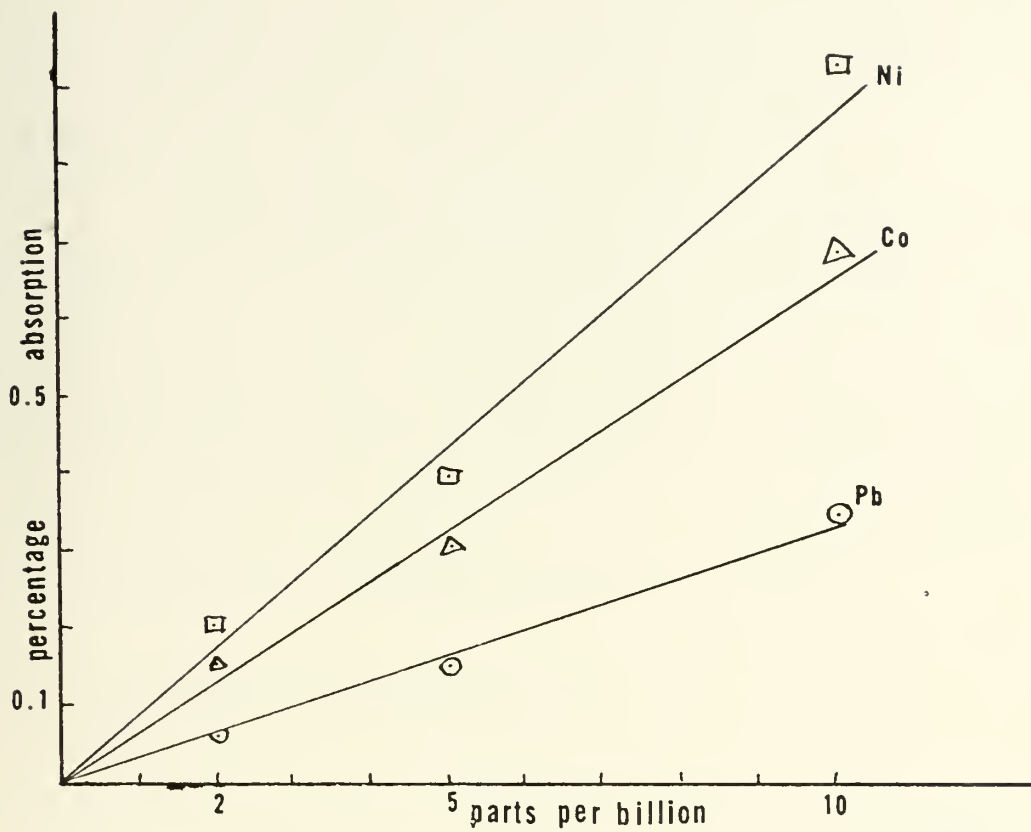


Figure 5

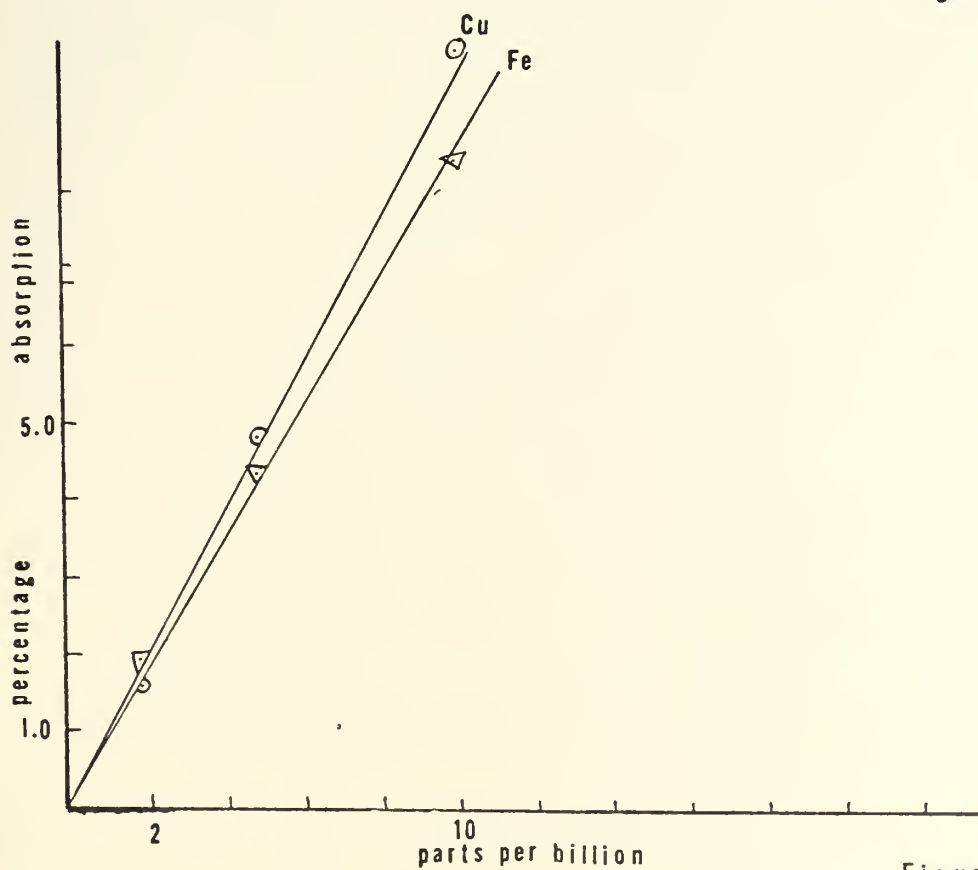


Figure 6

and a lean air-acetylene flame. Standard hollow cathode lamps were used for all of the elements. The instrument settings used in this analysis are given in Table I.

The percentage absorption for each sample at the wavelength of analysis was read directly from the atomic absorption unit. The absorption values for the standard solutions were used to construct working curves showing the relation between absorption and concentration (Figures 5 and 6). The concentrations of the desired elements in the unknowns were determined using these curves.

C. ANALYSIS BY POLAROGRAPHY

The trace metals were chelated with APDC and extracted into MIBK as described above. After the 30 minute equilibration and the separation of the phases, the organic phase (volume approximately 20 ml.) was combined with 20 ml. of 0.1N KCl solution with a pH of one. This solution was shaken for fifteen minutes and the phases were separated. The aqueous phase was placed into a polyethylene bottle and the organic phase was discarded. Prior to polarographic analysis, nitrogen was bubbled through the sample for ten minutes to remove dissolved oxygen. Since oxygen can be reduced at the cathode, it will cause interference unless it is removed.

Analysis was performed using a Sargent Recording Polarograph, Model XV, with a dropping mercury electrode. The mercury was allowed to drop at the rate of one drop every four seconds. Solutions

of 0.5 parts per million and 1.0 parts per million of cobalt, copper, iron, lead, and nickel in a 0.1N KCl solution were prepared and used as standards.

The polarograms were interpreted using the geometrical method described in Pinta (1970). At the points of inflection (A and B) tangents were drawn to the portions of the polarization curve immediately preceding and following the diffusion wave (Figure 7). The distance CE between these tangents is measured along a line, parallel to the ordinate, which passes through the point of inflection D and the reduction of half-wave potential ($E_{1/2}$) of the ion. This distance is proportional to the diffusion current which in turn is proportional to the concentration of the ion reduced at the potential $E_{1/2}$. A graph of diffusion current versus concentration was prepared for the elements in the standard solutions and used as the working curve for the determination of the concentrations of trace metals in the unknown samples (Figure 8).

It was attempted to determine the efficiency of the extraction procedure used prior to polarographic analysis by applying the technique to a solution of known concentration. A solution containing 20 parts per billion of cobalt, copper, iron, lead, and nickel was prepared in double distilled water, extracted using the above method and analysed by polarography using the same instrumental parameters as were used for the other samples. The results are discussed below.

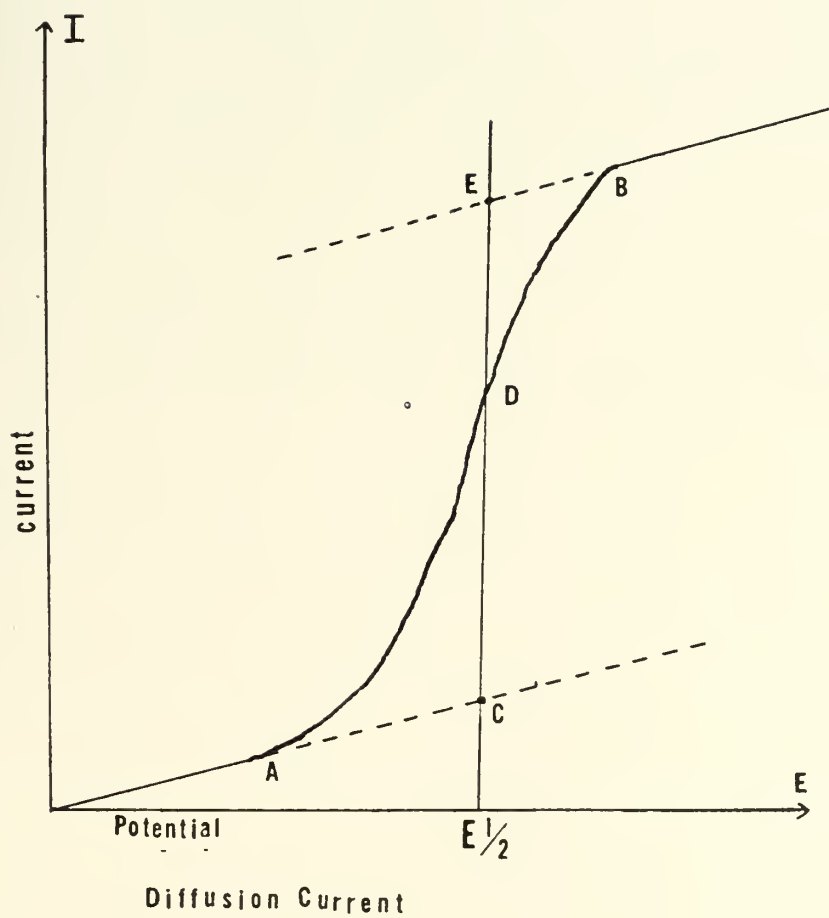


Figure 7

Pinta (1970)

IV. PRESENTATION OF DATA

A. DATA FROM ATOMIC ABSORPTION SPECTROPHOTOMETRY

The concentrations of the heavy metals cobalt, copper, iron, lead and nickel in the water off Del Monte Beach as determined by atomic absorption spectrophotometry are summarized in Table II. The zero of the working curves (Figures 5 and 6) were taken as the blank. The raw data, in the form of percentage absorption, is included in Appendix A.

B. DATA FROM POLAROGRAPHY

Utilizing the APDC-MIBK solvent extraction system as a concentration procedure prior to analysis by polarography was found to permit determination of only one of the desired elements. The diffusion wave of lead at -0.435 volts was visible in the polarograms of the solutions analysed by this technique. However, the diffusion waves of the other four elements were masked by interferences. The concentrations of lead in the water off Del Monte Beach as determined by polarography are presented in Table III. The polarograms are reproduced in Appendix B.

TABLE I

Instrument Parameters for Atomic Absorption						
<u>Metal</u>	<u>Wavelength</u>	<u>Slit Setting</u>	<u>Line Pressure</u>		<u>Load Pressure</u>	
			<u>Air</u>	<u>Fuel</u>	<u>Air</u>	<u>Fuel</u>
cobalt	241	3	17	8	5	1.5
copper	325	4	30	8	11.5	1.5
iron	249	2	30	8	11.5	1.5
lead	283	4	17	8	5	1.5
nickel	352	3	30	8	11.5	1.5

TABLE II

Trace Elements in Sea Water Off Del Monte Beach
(concentration, ppb.)

<u>Station</u>	<u>Cobalt</u>	<u>Copper</u>	<u>Iron</u>	<u>Lead</u>	<u>Nickel</u>
A2	6.0	17.4	2.9	7.4	0.5
A4	4.6	17.8	2.3	6.8	0.7
B3	7.5	16.2	2.1	8.8	0.6
C2	4.6	15.7	2.5	6.4	0.3
C4	4.4	17.0	2.3	6.8	0.3
D3	7.0	15.6	2.3	7.4	0.5

TABLE III

Concentration of Lead in Sea Water by Polarography

Station	A2	A4	B3	C2	C4	D3
ppb Pb.	16	11	26	13	32	---

V. CONCLUSION

A. DISCUSSION OF RESULTS

Brewer et al. (1969) state that the concentrations in the ocean of copper and nickel range from 0.07 to 10 parts per billion and from 1.0 to 20 parts per billion respectively. The mean values for the abundance of iron and cobalt are 10 parts per billion and 0.1 parts per billion (Burrell 1968). The concentrations of cobalt, copper, and lead determined in the present study were somewhat higher than these expected values. This may be due to the close proximity of the study area to the city of Monterey, causing local enrichment in heavy metals.

The concentrations of iron and nickel were, on the other hand, lower than the expected values for these elements. The APDC complexes of iron and nickel are the least stable of the complexes formed with APDC by the five elements (Brooks et al. 1967). The minimum time for which they are stable is three hours. The time period between extraction of the metals and analysis by atomic absorption was little less than three hours for iron and a little more than three hours for nickel. The delay in analysis was caused by the necessity to prepare and extract the standard solutions and by the time needed to warm up the hollow cathode lamps for succeeding determinations. This delay may have been long enough so that the complexes of iron and nickel began to decompose. Therefore the

concentrations determined by atomic absorption might be lower than the actual values for iron and nickel.

The APDC-MIBK extraction system was found to be unsuitable as a pre-analysis concentration procedure for polarography. When a polarogram was made of 1% APDC in 0.1N KCl at a pH of one, it showed a strong signal from -0.6 volts to -2.0 volts. This signal would interfere with the determinations of the metals cobalt, iron, and nickel whose diffusion waves are located in this range (Pinta 1970). An interference at -0.2 volts obscured the diffusion wave for copper. As seen in Table III, the values that were obtained for lead are erratic and higher than the values determined using atomic absorption. Since atomic absorption gives a total analysis and polarography gives an analysis only of the ionized species, the fact that the polarography values are higher than the atomic absorption values is a further indication of the inapplicability of the APDC-MIBK solvent extraction system to polarographic analysis.

B. SUGGESTIONS FOR FURTHER RESEARCH

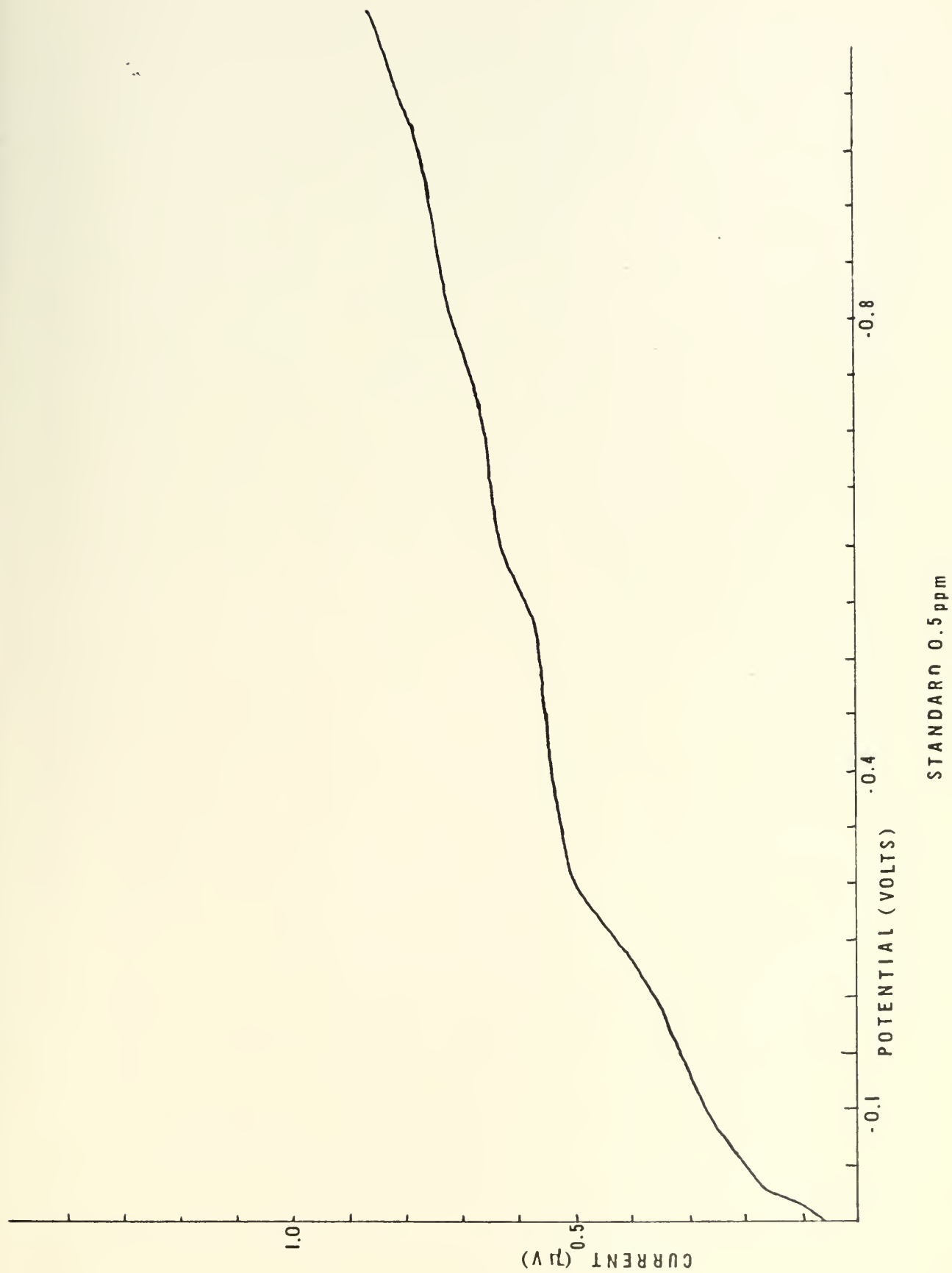
It would be useful to repeat the determination of these five heavy metals in the water of the breakwater area after completion of the breakwater. The APDC-MIBK solvent extraction procedure with atomic absorption can be recommended for this purpose. Investigation of concentration techniques other than the APDC-MIBK extraction system for polarography might be applied to the problem.

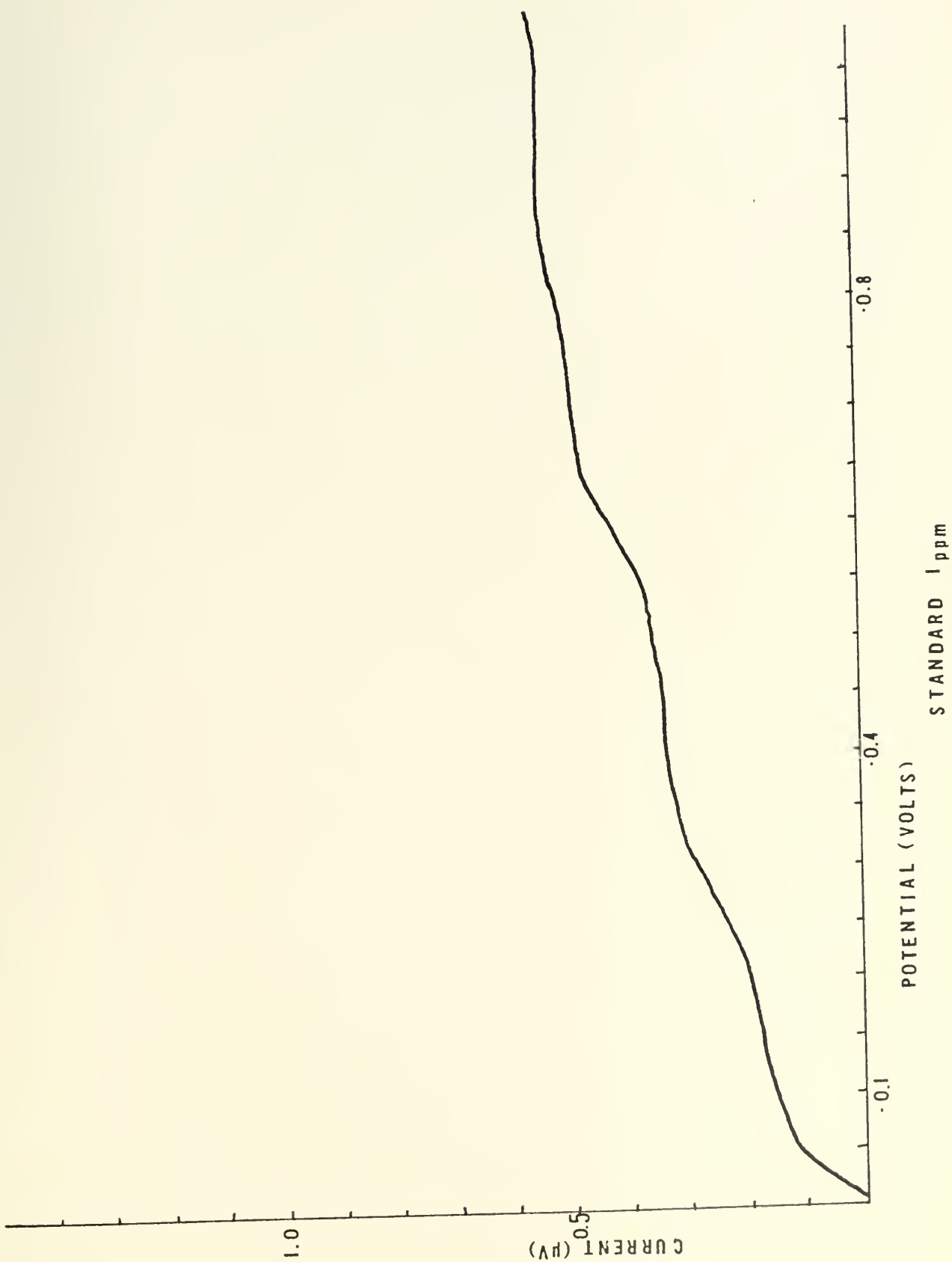
If the changes in the ecology of the area are to be monitored, it is important also to monitor the changes in the chemical environment brought about by harbour construction. A study of the chemical environment coupled with a study of species diversity may yield new insights into the relationship between an organism and its surroundings.

APPENDIX A

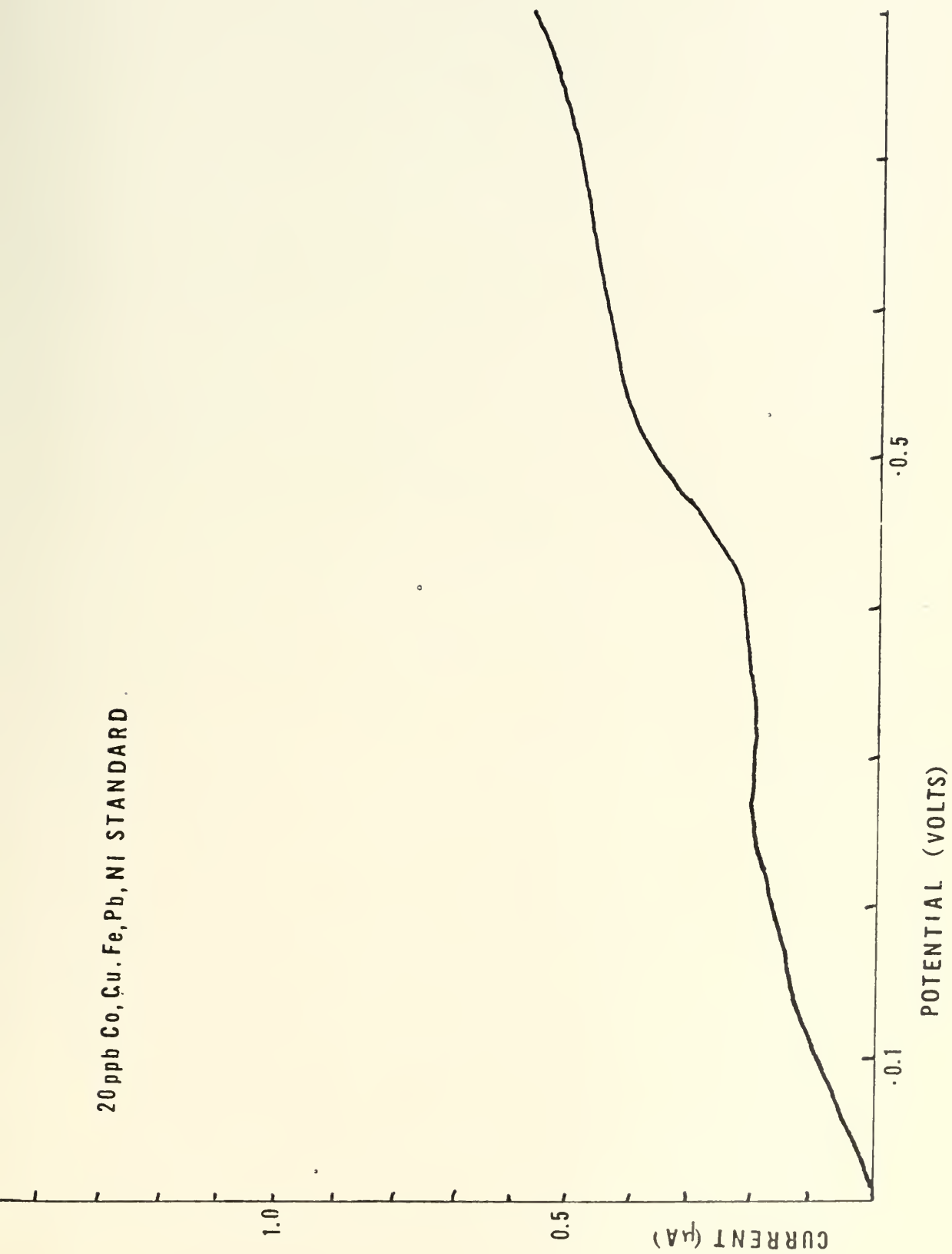
Percentage Absorption Values

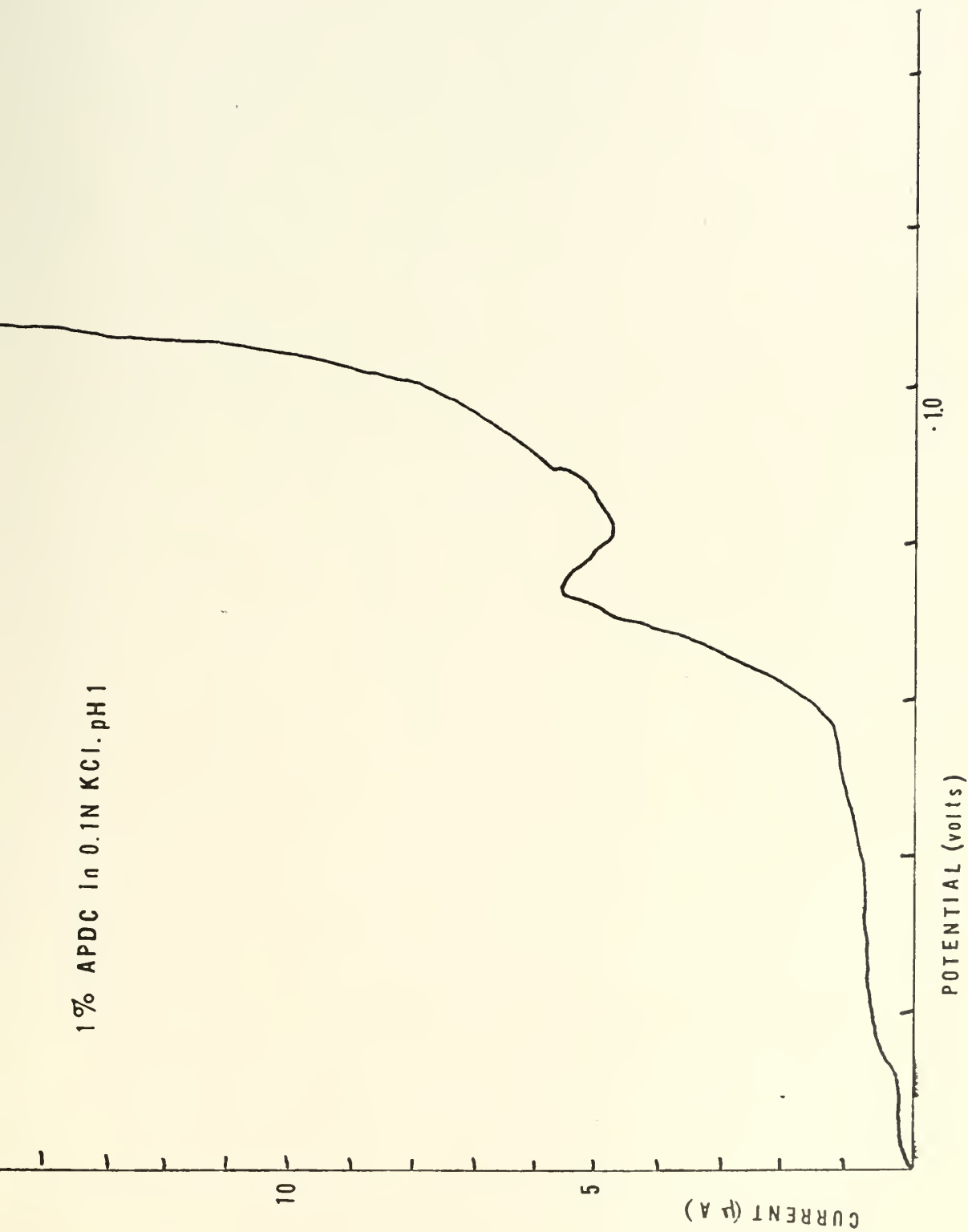
<u>Standards</u>	<u>Cobalt</u>	<u>Copper</u>	<u>Iron</u>	<u>Lead</u>	<u>Nickel</u>
0ppb	0.00	0.00	0.00	0.00	0.00
2 ppb	0.16	1.60	1.90	0.06	0.20
5 ppb	0.30	4.90	4.50	0.15	0.40
10 ppb	0.68	9.90	8.50	0.35	0.93
<u>Unknowns</u>					
A2	0.42	16.6	2.56	0.24	0.04
A4	0.32	17.0	2.06	0.22	0.06
B3	0.52	15.5	1.80	0.28	0.05
C2	0.32	15.0	2.16	0.20	0.03
C4	0.30	16.3	2.06	0.22	0.03
D3	0.48	14.9	2.00	0.24	0.04





20 ppb Co, Cu, Fe, Pb, Ni STANDARD





STATION A2

CURRENT (A)

POTENTIAL (VOLTS)

0.5

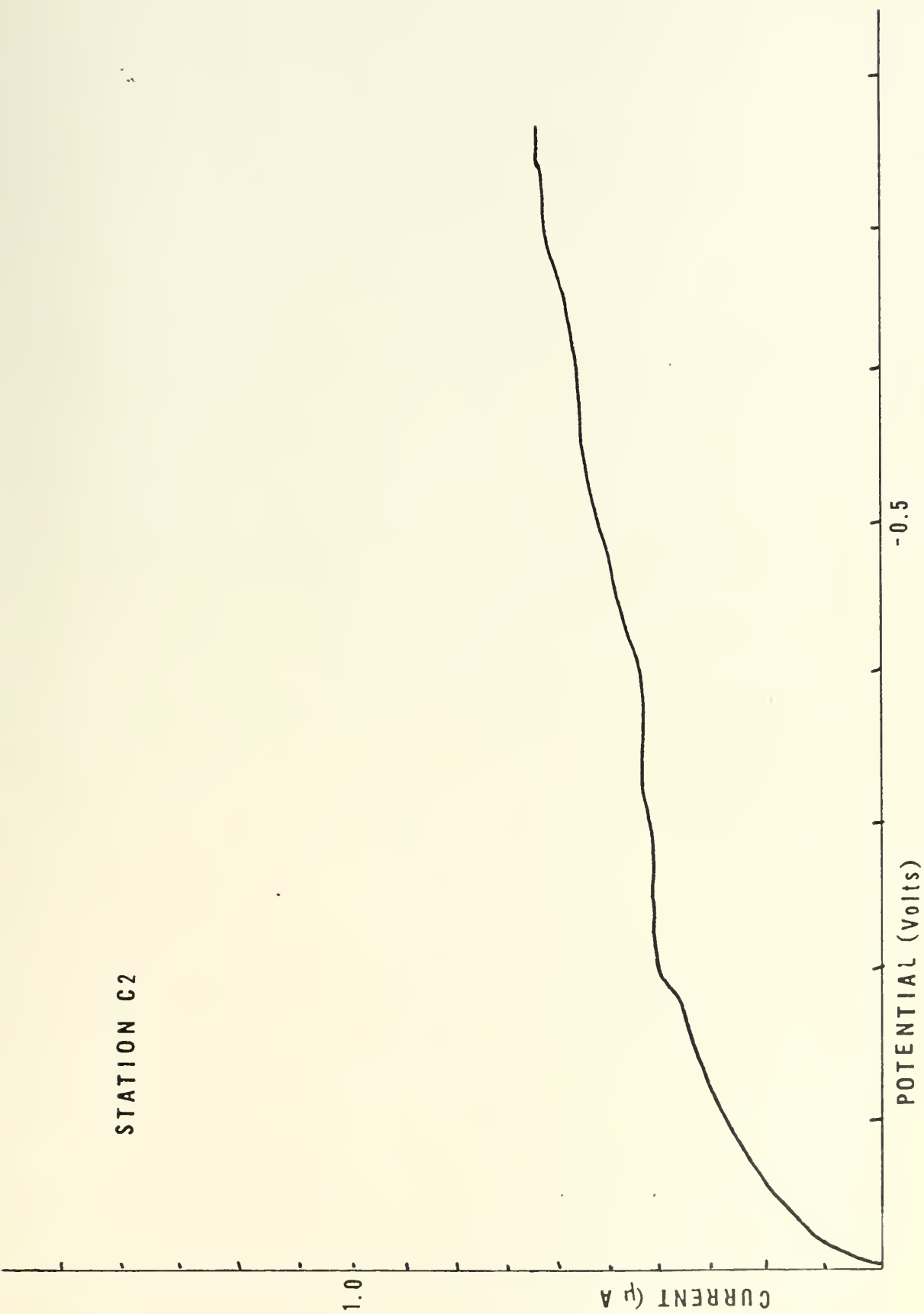
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13. ABSTRACT <p>As part of the Monterey Breakwater Project, six water samples were taken from the study area located offshore from Del Monte Beach east of Municipal Wharf No. 2 in Monterey, California. The heavy metals in the sea water were concentrated and removed using the ammonium pyrrolidine dithiocarbamate (APDC) -- methyl isobutyl ketone (MIBK) solvent extraction system. The concentrations of the metals cobalt, copper, iron, lead, and nickel in the samples were determined using atomic absorption spectrophotometry. It was found that the APDC-MIBK solvent extraction system was not adequate for analysis by polarography.</p>			

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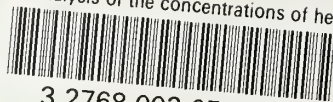
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